

# Does Singlet Fission Enhance the Performance of Organic Solar cells?

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(Dated: September 21, 2012)

Singlet fission, in which the optical spin-singlet exciton dissociates into two low energy triplet excitons, has been proposed as a viable approach to enhance the quantum efficiency of organic solar cells. We show that even when singlet fission is occurring in the donor molecule, the electronic structure at the donor-acceptor interface must satisfy specific requirements for the solar cell performance to be enhanced by this process. We focus on the pentacene- $C_{60}$  solar cell and based on our calculations and available experimental data we conclude that there is not enough evidence that these requirements are met by the donor-acceptor interface here. We propose experiments that can determine whether the minimal requirement for enhanced performance driven by singlet fission is met in this and other solar cells.

## Introduction

Multiple exciton generation (MEG), involving the generation of two or more low energy excitons from the absorption of a single high energy photon<sup>1</sup>, has been suggested as an important means to overcome the Shockley-Queisser upper limit of 33%<sup>2</sup> for the quantum efficiency (QE) of inorganic solar cells. Within the MEG scenario, an optically generated high energy exciton undergoes conversion to several lower energy excitons, while obeying energy conservation. If each of the low energy excitons now undergoes dissociation into electron and hole carriers, the QE will exceed the limit for a single exciton. A related process, singlet fission (SF), has generated considerable excitement in the context of organic solar cells<sup>3-17</sup>. In organic  $\pi$ -conjugated materials, total spin is usually a good quantum number, and exchange interactions are large. The spin selection rule limits optical absorption to spin singlet states only, with most of the oscillator strength concentrated in the lowest optical exciton in the quasi-one-dimensional materials<sup>18,19</sup>. It has long been recognized that in many  $\pi$ -conjugated systems, the energies of the optical spin singlet state and the lowest triplet state satisfy the inequality  $E_S \geq 2E_{T_1}$ , where  $E_S$  ( $E_{T_1}$ ) is the singlet (triplet) exciton energy. Indeed, in many such systems, the lowest singlet state is not the optical exciton, but an optically forbidden two-photon state that is an entangled state of two triplets (hereafter TT)<sup>20-22</sup>. In principle, such a system is a candidate for SF, whereby the singlet optical exciton undergoes fission into two triplet excitons. While SF in organic materials has been known for a long time<sup>23</sup>, recent excitement began with the observation of relatively high power conversion efficiency of organic solar cells with pentacene (hereafter PEN) as the donor ( $D$ ) molecule and  $C_{60}$  as the acceptor ( $A$ )<sup>24,25</sup>. Experimental demonstrations of SF in tetracene and pentacene crystals<sup>3-6,11,16,17,26-32</sup>

have led to the idea that the enhanced performance of PEN- $C_{60}$  solar cells is due to SF.

With few exceptions<sup>6,16</sup>, research on SF has largely focused on the determination of the mechanism of SF in the acenes<sup>3-5,7-12,23,26-31</sup>. Whether or not SF can give enhanced performance, however, depends on the electronic structures of both  $D$  and  $A$ , and in particular, of the  $D$ - $A$  interface. The goal of our work is different from the bulk of the existing theoretical work on SF<sup>7-10,12</sup> and is complementary to this research; it is to determine *the conditions which need to be satisfied for SF-driven higher QE in organic solar cells*.

At the heart of organic photovoltaics lies photoinduced charge-transfer (PICT) between  $D$  and  $A$  at their interface. Optically excited  $D$  ( $A$ ) donates an electron (hole) to its partner, generating a charge-transfer exciton  $D^+A^-$ . The lowest energy charge-transfer exciton (hereafter CTX<sub>0</sub>), depending upon its binding energy, now undergoes recombination as well as charge-separation, and only the latter process is useful in photovoltaics. For SF to give enhanced photovoltaic performance, each of the two molecular triplets should now donate an electron or a hole to its partner. One then sees right away that for SF-driven higher performance each of the following conditions have to be satisfied: (i)  $E_{CTX_0} \leq E_{T_1}$ , where  $E_{CTX_0}$  is the energy of the lowest charge-transfer exciton, (ii) the binding energy of CTX<sub>0</sub> should not be prohibitively large, and (iii) the ground-state should continue to be neutral covalent and should not have undergone transition to an ionic state (such neutral-to-ionic transition, for example, occurs in crystalline mixed-stack charge-transfer solids<sup>33</sup>.) Note that condition (i) requires a very low energy CTX<sub>0</sub>, given that  $E_{T_1}$  should satisfy  $E_S \geq 2E_{T_1}$ . Indeed, such low energy triplets are covalent in the valence bond language<sup>21,22</sup>, suggesting their unsuitability in charge-transfer processes. Conditions (ii) and (iii) have to be therefore satisfied

in spite of the very low  $E_{\text{CTX}_0}$ .

In the work presented here, we report explicit calculations of PICT on the PEN- $\text{C}_{60}$  system. We show from comparisons of detailed calculations and available experimental information that whether or not SF in PEN is expected to give higher performance of the PEN- $\text{C}_{60}$  solar cell is not at all obvious. Even if SF-driven enhanced performance is occurring in this system, we show that PEN- $\text{C}_{60}$  is a marginal case where the above conditions are barely satisfied, and it cannot be assumed that all the molecules<sup>9</sup> that are being investigated as candidates for SF will necessarily lead to higher QE for PICT. Elaborate evaluations of the above conditions for each  $D$ - $A$  pair are essential, since for systems in which they are not satisfied, SF provides a competing channel for the decay of the photoexcitation and diminished performance.

In the next section we present our theoretical model and discuss the computational approach we have taken to simulate the PEN- $\text{C}_{60}$  interface, and to determine the binding energy of  $\text{CTX}_0$ . Following this, we present our results, for parameters appropriate for isolated PEN and  $\text{C}_{60}$  molecules, as well as for the solid state heterostructure. Although our principal goal is to determine trends and to provide insight, we show that our calculations reproduce many of the known experimental results almost quantitatively. This is because our parameterization of the PPP Hamiltonian has been done with considerable care<sup>34</sup>. Our calculated absolute exciton energies as well as the exciton binding energies in single-walled carbon nanotubes<sup>35</sup>, and of one and two-photon states in polycyclic hydrocarbons that are molecular fragments of graphene<sup>36</sup> have shown similar quantitative agreement between theory and experiment. We present the results for the energetics of the charge-transfer excitons for the PEN- $\text{C}_{60}$  interface, and its binding energy, for a geometry that should be maximally favorable for PICT. Based on these computational results, and additional work on the extent of charge-transfer in the ground-state presented in the Appendix, we present our conclusions in the final section.

### Theoretical Model and Methods.

We have performed correlated-electron calculations for an idealized quasi-one-dimensional heterostructure with four PEN and three  $\text{C}_{60}$  molecules forming a perfect one-dimensional stack (4PEN-3 $\text{C}_{60}$  hereafter, see Fig. 1(a)). We assume the PEN molecules to lie directly above or below one another with an eclipsed geometry. We assume similarly that one hexagonal face of each  $\text{C}_{60}$  faces a

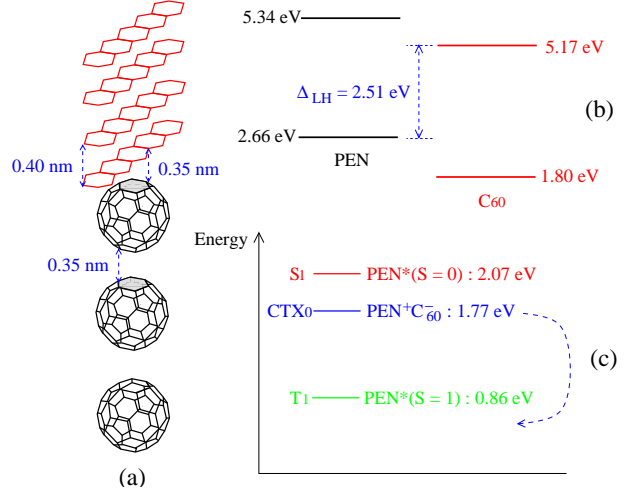


FIG. 1: (Color online) (a) Schematic of the PEN- $\text{C}_{60}$  “heterostructure” investigated in our work (see text); intermolecular separations are as indicated in the figure. (b) The PPP HOMO and LUMO energies of PEN and  $\text{C}_{60}$  within the HF approximation, and with our Coulomb interaction parameters; the  $\text{C}_{60}$  HOMOs and LUMOs are five and threefold degenerate, respectively. (c) Calculated energies of the singlet optical exciton in PEN and the lowest  $\text{PEN}^+\text{C}_{60}^-$  charge-transfer exciton, relative to the ground-state, using parameters appropriate for isolated PEN and  $\text{C}_{60}$ , and identical screening parameters for intra- and intermolecular Coulomb interactions. The energy of the triplet  $T_1$  is from experiment<sup>28</sup>. For SF to give enhanced solar cell efficiency, the lowest charge-transfer exciton should occur below  $T_1$ , as the curved arrow in the figure indicates.

hexagonal face of the next  $\text{C}_{60}$  molecule, with all intermolecular carbon atoms perfectly aligned. Finally, a hexagonal face of the top  $\text{C}_{60}$  molecule is assumed to be perfectly aligned with the central benzene nucleus of the proximate PEN molecule (see Fig. 1(a)). The minimum separations between two  $\text{C}_{60}$  molecules as well as that between the closest PEN and  $\text{C}_{60}$  are 0.35 nm in our calculations, while that between the PEN molecules are taken to be 0.40 nm. These separations are representative of intermolecular separations in organic molecular crystals (including, in particular, epitaxially grown films of  $\text{C}_{60}$  on  $\text{VSe}_2$ <sup>37</sup>). We are aware that the relative orientations between PEN and  $\text{C}_{60}$  are quite different in the real systems<sup>38,39</sup>, but have deliberately chosen this idealized conformation, since this will promote maximally stable CTX and most efficient charge separation, because of the large intermolecular hoppings that result from the idealized geometry. While recombination is also higher with this geometry<sup>40</sup>, this is not of concern here.

Our calculations are within the Pariser-Parr-Pople (PPP) Hamiltonian<sup>41,42</sup> for a two-component system<sup>43</sup>,

$$H = H_{intra} + H_{inter} \quad (1)$$

The intramolecular component  $H_{intra}$  is given by,

$$H_{intra} = - \sum_{\mu(ij),\sigma} t_{ij}^{\mu} (c_{\mu,i,\sigma}^{\dagger} c_{\mu,j,\sigma} + H.C.) + U \sum_{\mu,i} n_{\mu,i,\uparrow} n_{\mu,i,\downarrow} + \sum_{\mu,i < j} V_{ij} (n_{\mu,i} - 1)(n_{\mu,j} - 1) - \sum_{\mu=5-7,i,\sigma} \epsilon_{\mu} n_{\mu,i,\sigma}. \quad (2)$$

In the above  $c_{\mu,i,\sigma}^{\dagger}$  creates a  $\pi$ -electron of spin  $\sigma$  on carbon atom  $i$  of molecule  $\mu$ , with  $\mu = 1 - 4$  corresponding to PEN, and  $\mu = 5 - 7$  corresponding to C<sub>60</sub>, respectively.  $n_{\mu,i,\sigma} = c_{\mu,i,\sigma}^{\dagger} c_{\mu,i,\sigma}$  is the number of electrons on atom  $i$  of molecule  $\mu$  with spin  $\sigma$  and  $n_{\mu,i} = \sum_{\sigma} n_{\mu,i,\sigma}$  is the total number of electrons on atom  $i$  of the molecule.  $U$  and  $V_{ij}$  are the on-site and intramolecular intersite Coulomb interactions, respectively. The  $V_{ij}$  are obtained from a modification of the Ohno parameterization<sup>44</sup>,

$$V_{ij} = U/\kappa \sqrt{1 + 0.6117 R_{ij}^2}, \quad (3)$$

where  $R_{ij}$  is the distance between carbon atoms  $i$  and  $j$  in Angstroms and  $\kappa$  is an effective dielectric constant. Previous work has shown that  $U = 8$  eV and  $\kappa = 2$  give excellent fits to absolute exciton energies as well as exciton binding energies in the  $\pi$ -conjugated polymer poly-paraphenylenevinylene<sup>34</sup> and single-walled carbon nanotubes<sup>35</sup>. We have used standard nearest neighbor one-electron hopping integrals  $t_{ij}^{\mu} = 2.4$  eV for phenyl C-C bonds in PEN<sup>34</sup>, and  $t_{ij}^{\mu} = 1.96$  eV and 2.07 eV, respectively, for the bonds within the pentagons of C<sub>60</sub> and for those linking the pentagons. The smaller C<sub>60</sub> hopping integrals reflect the curvature that reduces the overlap between neighboring  $p$ -orbitals<sup>35</sup>. We show below that excellent fits to various energy gaps of isolated PEN and C<sub>60</sub> are obtained with these parameters.

The intermolecular component  $H_{inter}$  of the Hamiltonian is written as,

$$H_{inter} = - \sum_{\mu < \mu', i, j, \sigma} t_{ij}^{\perp} (c_{\mu,i,\sigma}^{\dagger} c_{\mu',j,\sigma} + H.C.) + \frac{1}{2} \sum_{\mu < \mu', i, j} V_{ij}^{\perp} (n_{\mu,i} - 1)(n_{\mu',j} - 1). \quad (4)$$

We use the same functional form for  $V_{ij}^{\perp}$  as for the intramolecular Coulomb interaction with however a dielectric constant  $\kappa_{\perp}$  that may be different

from  $\kappa$  (smaller  $\kappa_{\perp}$  implies greater intermolecular interaction). Intermolecular hopping integrals follow  $t_{ij}^{\perp} = \beta \exp[(c - d_{ij})/\delta]$ , where the prefactor  $\beta = 0.2$  eV,  $c$  is the minimum vertical distance between the molecules,  $d_{ij}$  is the distance between atom  $i$  belonging to molecule  $\mu$  and atom  $j$  belonging to molecule  $\mu' \neq \mu$  and the decay constant  $\delta = 0.045$  nm<sup>43,45</sup>.

The last term in Eq. 2 contains a site energy  $\epsilon_{\mu}$  that is nonzero only for the atoms of the C<sub>60</sub> molecules, and that is included to manipulate the energy offsets between the molecular orbitals (MOs) of PEN and C<sub>60</sub>, in order to vary the energy of CTX<sub>0</sub>. The energy of the charge-transfer exciton in an arbitrary  $D$ - $A$  system, in the limit of zero intermolecular hopping, is approximately given by<sup>46</sup>  $IE_D - EA_A - E_C$ , where  $IE_D$  is the ionization energy of  $D$ ,  $EA_A$  is the electron affinity of  $A$  and  $E_C$  is the Coulomb stabilization energy due to proximate oppositely charged  $D$  and  $A$  in  $D^+A^-$ . This concept in the past has been used mostly for molecular  $D$  and  $A$  with nondegenerate highest occupied molecular orbital (HOMO) and lowest unoccupied MO (LUMO). Very interestingly, we find that it is equally well applicable here, with fivefold degenerate HOMO and threefold degenerate LUMO in C<sub>60</sub> (see below).  $IE_D$  and  $EA_A$  are both one-electron quantities, and their values in the gas phase and in the solid state can differ widely. We simulate the modifications of  $IE_D - EA_A$  in the solid state empirically by the effective site energy  $\epsilon_{\mu}$ , which modulates the mean-field Hartree-Fock (HF) energy difference between the LUMO of the acceptor and HOMO of the donor, in accordance with Koopman's theorem. We shall refer to this energy difference as  $\Delta_{LH}$  in what follows (*i.e.*,  $\Delta_{LH} = IE_D - EA_A$ ). The Coulomb stabilization energy  $E_C$  on the other hand originates from the  $V_{ij}^{\perp}$  in Eq. 4.

Our calculations are mostly within the single configuration interaction (SCI) scheme, including CI between all one electron - one hole excitations from the HF ground-state, which we take to be a product function of the HF ground-states of the individual molecules. This approach enables us to determine ionicities of excited states quantitatively<sup>43</sup>, and also the location of the excited electron and hole in a charge-transfer state. As we show below, this ability to precisely characterize all excited states allows us to determine the binding energy of CTX<sub>0</sub> for the model system we are considering. Finally, the SCI assumes the ground-state to be neutral and whether or not there is ground-state charge-transfer cannot be determined using this approach. We report separate full CI calculations on simpler model systems (see Appendix) to demonstrate

that conditions  $E_S \geq 2E_{T_1}$  and  $E_{CTX_0} \leq E_{T_1}$  can be simultaneously satisfied even with a neutral ground-state.

## Results

We begin with computational results for the case where HOMO-LUMO offsets between PEN and  $C_{60}$  are assumed to be the same as in the gas phase ( $\epsilon_\mu = 0$ ) and the screening parameter for the intermolecular Coulomb interactions is assumed to be the same as for the intramolecular interactions ( $\kappa_\perp = \kappa$ ). Following this we simulate solid state effects by performing calculations for nonzero  $\epsilon_\mu$  and varying  $\kappa_\perp$ . Finally, we report calculations of the binding energy of  $CTX_0$  as a function of  $\epsilon_\mu$  and  $\kappa_\perp$ .

PEN- $C_{60}$  interface with “gas phase”  $\Delta_{LH}$ . In Figs. 1(b) and (c) we have given our results for isolated molecules. Fig. 1(b) shows the calculated HF HOMOs and LUMOs of PEN and  $C_{60}$ . Our calculations are within the  $\pi$ -electron approximation, and the absolute HOMO and LUMO energies are not meaningful. However, all energy *differences*, including the calculated  $\Delta_{LH}$ , are relevant. Fig. 1(c) shows the main result for the PEN- $C_{60}$  interface, using the MO energies and wavefunctions corresponding to Fig. 1(b) and  $\kappa_\perp = \kappa = 2$ . Thus the results of Fig. 1(c) correspond to the assumption that the molecular HF energies and wavefunctions are not perturbed at all at the interface in the solid state. Our calculations are for the singlet states only and the energy of the triplet exciton is taken from experiment<sup>28</sup>.

There are several items of interest in the results shown in Figs. 1(b) and (c). Our calculated energy of the optical exciton in PEN, 2.10 eV, is extremely close to the experimental energy of 2.07 eV in solution<sup>30</sup>. Our calculated HOMO-LUMO gap for  $C_{60}$  3.37 eV is practically the same as the experimentally determined value of 3.36 eV<sup>37</sup>. The calculated energies for the two lowest allowed optical absorptions in the gas phase of  $C_{60}$ , 3.1 and 3.5 eV (not shown) are also very close to the experimental values 3.0 and 3.6 eV respectively for  $C_{60}$  molecules dissolved in decalin<sup>47</sup>. All of these give confidence that our computational approach and the parameters used reproduce the behavior of the individual molecules almost quantitatively. Our calculated  $E_{CTX_0}$  of 1.77 eV, taken together with the calculated  $\Delta_{LH} = 2.50$  eV indicates that  $E_C$  is close to 0.7 eV, provided the assumption that the approximate expression  $E_{CTX_0} = \Delta_{LH} - E_C$  is valid holds here. This value of  $E_C$  is slightly *larger* than

that calculated from electrostatic considerations for  $PEN^+C_{60}^-$  at an intermolecular distance of 0.35 nm (see Fig. 5 in Reference 40). Had we evaluated  $E_{CTX_0}$  from  $IE_D - EA_A - E_C$ , using the known “bare” ionization energy of PEN 6.59 eV<sup>48</sup> and bare electron affinity of  $C_{60}$  2.68 eV<sup>49</sup>, along with the calculated  $E_C$  of Reference 40, the calculated quantity would have been significantly larger than the 1.77 eV obtained by us. It is then reasonable to hold our calculated  $E_{CTX_0}$  as a realistic *lower limit* for the energy of the charge-transfer exciton with gas phase parameters. As indicated in Fig. 1(c), enhanced QE due to SF is not expected here. The curved broken arrow indicates the extent to which the energy of  $CTX_0$  needs to be lowered for SF to give higher QE. Smaller  $\Delta_{LH}$  and/or larger  $E_C$  than in the gas phase would be necessary for this.

Simulation of solid state effects. Smaller  $\Delta_{LH}$  in the solid state is a consequence of the smaller ionization energy of PEN and the larger electron affinity of  $C_{60}$  in the solid state. As mentioned in section II, we simulate solid state effects phenomenologically by varying  $\epsilon_\mu$ . In Fig. 2 we show the calculated  $E_{CTX_0}$  as a function of  $\epsilon_\mu$  for several different  $\kappa_\perp$  that enter into the calculations of  $V_{ij}^\perp$ . The linear variation of  $E_{CTX_0}$  with  $\epsilon_\mu$  is surprising, as this indicates that the simple expression  $E_{CTX_0} \simeq IE_D - EA_A - E_C$  continues to hold for a broad range of  $\epsilon_\mu$  and  $\kappa_\perp$ , even for nondegenerate HOMO and LUMO in  $C_{60}$  and with nonzero electron hoppings between PEN and  $C_{60}$ . It is conceivable that this is unique to  $C_{60}$  as the acceptor, since there can be few direct C-C intermolecular hoppings in this case. For each  $\kappa_\perp$  there exists a critical site energy  $\epsilon_\mu^c$  at which  $E_{CTX_0} < E_{T_1}$ .

The linear variations of  $E_{CTX_0}$  in Fig. 2 indicate that  $\Delta_{LH}$  also varies linearly with  $\epsilon_\mu$ . From the calculated  $\epsilon_\mu^c = 0.89$  eV for  $\kappa_\perp = 2$  (Fig. 2) we find that the critical  $\Delta_{LH}$  at which  $E_{CTX_0} < E_{T_1}$  is  $\sim 1.6$  eV for the case where intra- and intermolecular screening are comparable. We conclude that the lowest  $PEN^+C_{60}^-$  charge-transfer exciton will be above the lowest triplet exciton unless at least one of the following two conditions are met (i)  $\Delta_{LH} < 1.6$  eV (ii)  $|E_C| > 0.7$  eV.

## Binding energy of the lowest charge-transfer exciton.

Our definition of the binding energy of  $CTX_0$ ,  $E_b$ , is the usual one: it is the energy difference between  $CTX_0$  and the lowest state in which the hole on the PEN molecules and the electron on the  $C_{60}$  molecules are free. A relevant question to ask therefore is whether the very low energy of the  $CTX_0$  that satisfies  $E_{CTX_0} < E_{T_1}$  implies also

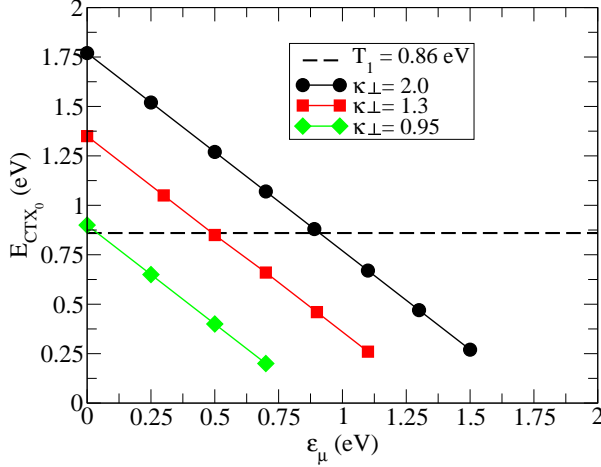


FIG. 2: (Color online)  $E_{\text{CTX}_0}$  versus  $\epsilon_\mu$ , the site energies on the carbon atoms of  $\text{C}_{60}$ , for different  $\kappa_\perp$ . The dashed line parallel to the abscissa is the experimental  $E_{T_1}$  from Reference 28.

a large binding energy. If true, this would also impact solar cell performance negatively. We have calculated  $E_b$  for our model heterostructure as a function of  $\epsilon_\mu$  to investigate this question.

The calculation of  $E_b$  is nontrivial, since in spite of the multiple PEN and  $\text{C}_{60}$  molecules retained in our calculations the overall system of Fig. 1(a) is still discrete and there is no true continuum. Thus the binding energy cannot be determined from energy considerations. We determine the threshold of the continuum from wavefunction analysis. We identify a specific high energy CT exciton with widely separated and delocalized electron and hole as the lower threshold of the continuum, and calculate the energy difference between this state and  $\text{CTX}_0$  as the lower bound for  $E_b$ . The wavefunction analysis is however complicated because in addition to states with complete charge-transfer there occur in the same energy range many other excited states including neutral  $\text{C}_{60}$  optically dark states and states with incomplete charge-transfer<sup>43</sup>. We ignore these additional irrelevant states and consider only excited states with at least 90% charge-transfer.

In Fig. 3(a) we show schematics of  $\text{CTX}_0$  and the high energy charge-transfer exciton, hereafter  $\text{CTX}_n$ , that we use in our evaluation of  $E_b$ . The arrows indicate charge-transfer from the PEN molecules to the  $\text{C}_{60}$  molecules identified in the figure. The hole in  $\text{CTX}_0$  is delocalized over two PEN molecules, with the electron on the nearest  $\text{C}_{60}$ . The hole and the electron are both delocalized in  $\text{CTX}_n$  which has relatively weak contribution from configurations with the electron on the  $\text{C}_{60}$  nearest

to the PEN- $\text{C}_{60}$  boundary. *The wavefunctions of these excitons are nearly independent of  $\epsilon_\mu$  and  $\kappa_\perp$ .* In Fig. 3(b) we have plotted the energy difference between higher energy charge-transfer excitons and  $\text{CTX}_0$  against the quantum number of the former, for  $\kappa_\perp = 2$  and  $\kappa_\perp = 0.95$ , and for several different  $\epsilon_\mu$  in each case. The terminal points for all curves correspond to  $\text{CTX}_n$ . The consequence of smaller  $\Delta_{\text{LH}}$  (larger  $|\epsilon_\mu|$ ) is to shift the quantum number of charge-transfer states relative to the “irrelevant” neutral states, but has no bearing on their energies.

The exciton binding energy  $E_b$  is independent of  $\epsilon_\mu$  for fixed  $\kappa_\perp$  as is shown in Fig. 3(c) for several different  $\kappa_\perp$ . This result has important *positive* implication for the effect of SF on the solar cell efficiency: if low energy for  $\text{CTX}_0$  is reached predominantly due to the reduction of the ionization energy of PEN and enhancement of the electron affinity of  $\text{C}_{60}$  in the PEN- $\text{C}_{60}$  heterostructure, the binding energy of  $\text{CTX}_0$  is not affected and continues to be small. Interestingly, our calculated binding energy for  $\text{CTX}_0$  (0.46 eV) for  $\kappa_\perp = 2$  is nearly identical to the estimation by Verlaak *et al.* (0.438 eV) from electrostatic considerations for the charge-transfer exciton in the PEN- $\text{C}_{60}$  heterostructure<sup>38</sup>. It is likely, however, that in a real three-dimensional structure this is somewhat smaller<sup>50,51</sup>.

The actual decrease in  $\Delta_{\text{LH}}$  due to solid state effects in the real system may not be sufficient to give  $E_{\text{CTX}_0} < E_{T_1}$  (see next section), in which case the lowering of  $E_{\text{CTX}_0}$  has to be driven by larger  $|E_C|$ . We have therefore calculated the critical  $\kappa_\perp$  required to obtain  $E_{\text{CTX}_0} < E_{T_1}$  for several different  $\Delta_{\text{LH}} > 1.6$  eV, and for each critical  $\kappa_\perp$  we have determined  $E_b$ . Our calculated results for  $E_b$  against  $\Delta_{\text{LH}}$ , now for different  $\kappa_\perp$  necessary to bring  $\text{CTX}_0$  below  $T_1$ , is shown in the inset of Fig. 3(d). We see that  $E_b$  increases dramatically and steeply as  $\kappa_\perp$  is reduced.

To summarize: (i) PPP calculations within the SCI approximation indicate that the approximate expression  $IE_D - EA_A - E_C$  for the lowest charge-transfer exciton is remarkably accurate for PEN- $\text{C}_{60}$  over a broad range of  $\epsilon_\mu$  and  $\kappa_\perp$ ; (ii) Low  $E_{\text{CTX}_0} < E_{T_1}$  in the solid state does not imply a high exciton binding energy of the  $\text{CTX}_0$  exciton if the lowering of its energy was primarily due to the smaller  $\Delta_{\text{LH}}$  in the solid state; (iii) on the other hand, if the lowering of the  $\text{CTX}_0$  energy is because of the larger intermolecular Coulomb interaction in the heterostructure, the binding energy will be substantially enhanced. Higher performance of the solar cell in the latter case is not expected, in spite of SF. Reviewing of the available experimental information, in particular of  $\Delta_{\text{LH}}$ , thus becomes

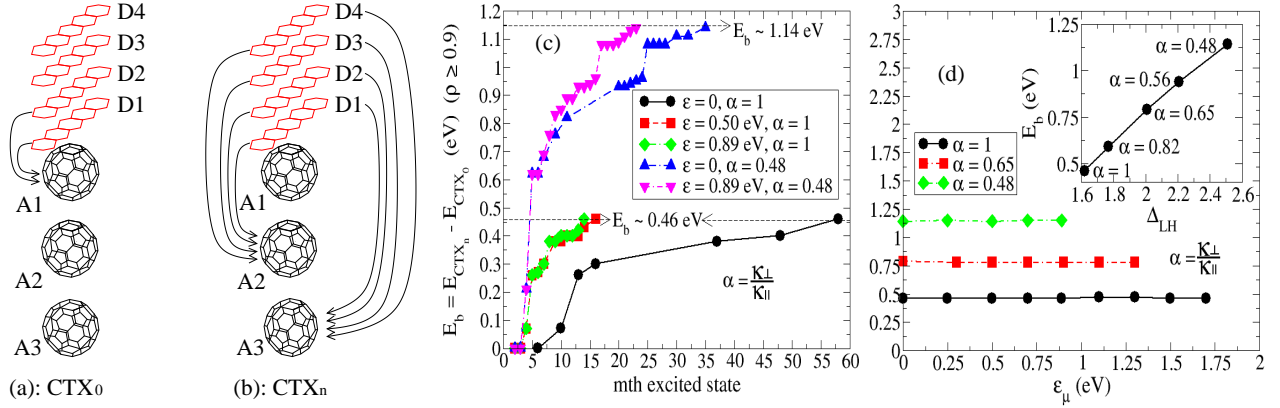


FIG. 3: (Color online) (a) Schematic of the lowest energy charge-transfer exciton CTX<sub>0</sub>. The arrows denote the lengths of the charge-transfer “bonds”. The wavefunction of CTX<sub>0</sub> is predominantly a superposition of the configuration with the hole on the PEN molecule and the electron on the C<sub>60</sub> molecule at the PEN-C<sub>60</sub> interface and the configuration with the hole on the neighboring PEN molecule. (b) Schematic of the high energy charge-transfer exciton CTX<sub>n</sub> with delocalized hole and electron. The arrows have the same meaning as in (a). (c) Energy differences between all higher energy charge-transfer excitons and CTX<sub>0</sub>, versus the quantum numbers of the higher excited states. The terminal point on each plot is CTX<sub>n</sub> of Fig. 3(b).  $\alpha = \kappa_\perp / \kappa_\parallel$  is a normalized measure of the inter- over intraunit screening. (d)  $E_b$  versus  $\epsilon_\mu$  for three different  $\alpha$ . The inset shows  $E_b$  against  $\Delta_{\text{LH}}$ , each with  $\alpha$  values required to satisfy  $E_{\text{CTX}_0} < E_{\text{T}_1}$ .

essential for determining whether or not SF is beneficial.

## Discussions

As mentioned in the Introduction, the bulk of the existing literature on SF is on single-component PEN, with the focus on understanding the mechanism of SF. To the best of our knowledge only three different groups have investigated the PEN-C<sub>60</sub> heterostructure in the context of SF<sup>6,14,16</sup>, and have concluded that SF indeed enhances charge generation. We reexamine aspects of these investigations carefully below, while emphasizing that our goal is *not* to claim that their conclusions are incorrect, but rather, to point out that further experimental and theoretical work is necessary to establish beyond doubt that SF is indeed behind the relatively large QE of PEN-C<sub>60</sub> solar cells<sup>24,25</sup>.

Among the works of interest, only the work by Lee *et al.* has made independent attempt to evaluate the QE of charge generation: the authors claimed 45% enhancement of the *external* QE for photocurrent generation in a PEN-C<sub>60</sub> multilayer photodetector, and ascribe this to enhanced *internal* QE due to SF in PEN<sup>6</sup>. This work is not based on the solar cell configuration, and it is not clear whether it is possible to predict solar cell performance from it. Furthermore, the estimation of the photocurrent efficiency was dependent upon various assumptions

and appears to be model dependent. Weak magnetic field dependence of the photocurrent upon laser excitation close to PEN absorption wavelength was observed, and was explained as due to reduction in the singlet character of the TT state in the presence of magnetic field. The TT singlet state is, however, a *quantum mechanical eigenstate of the full many-body Hamiltonian* and it is not clear why the nature of this wavefunction should change in the presence of a weak magnetic field. We conclude that while this work is of significant interest, additional independent measurements would be necessary to substantiate the principal claim of this work.

Rao and Wilson *et al.*<sup>16,17</sup>, and Chan *et al.*<sup>14</sup> actually have proposed very different mechanisms of electron transfer from the excited PEN state. Rao and Wilson *et al.*’s interpretation of their ultrafast spectroscopic measurements is the standard one, and the authors do believe that CTX<sub>0</sub> is below the triplet<sup>16,17</sup>. This latter conclusion is based upon an estimate of 4.5 eV for the EA of C<sub>60</sub> in the solid state<sup>52</sup>, which is larger by 1 eV compared to other estimates<sup>37</sup>. Such a large EA for C<sub>60</sub>, taken together with the solid state ionization energy of PEN (5.1 eV)<sup>55</sup> give a sufficiently small  $\Delta_{\text{LH}}$  that could actually lead to possible neutral-ionic transition in the ground state (see Appendix). Delayed charge generation is ascribed to longer triplet diffusion time to the heterojunction interface. Note, however that longer diffusion time is also expected

if the excited state in PEN is a superposition of TT and a PEN excimer<sup>53,54</sup>. Such a superposition in fact is suggested from theoretical work<sup>10</sup>. Standard one-electron transfer from the excimer component of the wavefunction is expected in this case, with the high QE (but less than one!) due to the long lifetime of the excimer and the ease of hole delocalization in PEN.

Chan *et al.*<sup>14</sup> have contradicted the scenario of single electron transfers from individual triplets and have proposed multiple electron transfers from either a quantum mechanical superposition of the PEN singlet exciton and the TT state (the authors refer to this last state as a multiexciton state and denote it as  $ME$ ), or from a related multiexciton state which they label as  $ME'$ . *The possibility that the  $ME$  or  $ME'$  state donates only one electron to one  $C_{60}$  molecule, is discarded by Chan *et al.* based entirely on the earlier work by Lee *et al.*<sup>6</sup>. Note that  $ME$  is also expected to have an excimer component<sup>10</sup>, which would make single-electron transfer from the excimer component of  $ME$  at least a likely channel. Assuming that the TT component of  $ME$  or  $ME'$  involves more than one PEN molecule<sup>7,8</sup> the proposed multi-electron transfer mechanism also requires  $E_{CTX_0} < E_{T_1}$ , since the multiexciton state needs to generate two charge-transfer excitons. It is this last requirement that we now examine below.*

Based on our computational results, we conclude that the upper limit for  $\Delta_{LH}$  that can give SF-enhanced performance is 1.6 eV. This is justified from the demonstration that  $E_b$  rises sharply for larger  $\Delta_{LH}$ . Note also that  $E_C$  calculated by others<sup>40</sup> is *smaller* than found by us, which would necessitate *even smaller*  $\Delta_{LH}$ . Coincidentally, the ionization energy of PEN in the solid state (5.1 eV)<sup>55</sup>, taken together with the electron affinity of  $C_{60}$  as measured by Schwedhelm *et al.* (3.5 eV)<sup>37</sup> gives  $\Delta_{LH}$  exactly equal to this critical value. It has, however, been demonstrated that the energy mismatch between levels in heterostructures cannot be obtained from studies of the individual semiconductors<sup>39</sup>. We are aware of only two references that have attempted to determine  $\Delta_{LH}$  based on experiments on the PEN- $C_{60}$  heterojunction<sup>56,57</sup> (as opposed to estimates based on experiments on isolated systems.) Kang *et al.*<sup>56</sup> find  $\Delta_{LH}$  of 1.56 eV and 1.50 eV, respectively, for  $C_{60}$  deposited on PEN (with gold as the substrate), and PEN deposited on  $C_{60}$  (also with gold as the substrate). Thus in both cases the measured  $\Delta_{LH}$  is considerably smaller than what would be obtained from  $EA$  of 4.5 eV for  $C_{60}$ <sup>52</sup> assumed in Reference 16, and would barely satisfy the necessary condition for enhanced QE. Significantly different  $\Delta_{LH}$  are found by Salzmann *et al.*,<sup>57</sup>

who find this quantity to depend strongly on the processing technique used to generate the heterostructure. For layered structures of  $C_{60}$  on PEN precovers PEDOT:PSS the authors find  $\Delta_{LH} \sim 1.15$  eV (see Fig. 3(a) of Reference 57), which would certainly make enhanced QE feasible. However, for codeposited films of PEN and  $C_{60}$  the authors determine  $\Delta_{LH} \sim 1.75$  eV (see Fig. 3(b) of Reference 57), which would make enhanced QE unlikely. Even more importantly, in both references only the HOMO energies of PEN and  $C_{60}$  are determined directly from experiments. The LUMO energy of  $C_{60}$  is estimated from the transport gap<sup>58</sup>. The latter approach makes the estimate of  $\Delta_{LH}$  questionable, as recent work has shown that the transport in molecular solids involves *intermolecular* charge-transfer states that can occur *below* the molecular LUMO level<sup>59</sup>. In the present case, while References 56 and 57 assume the HOMO-LUMO gap of solid  $C_{60}$  to be 2.6 eV, the same quantity is estimated to be 3.36 eV for epitaxial layers of  $C_{60}$  on layered  $VSe_2$  single crystals by Schwedhelm *et al.*<sup>37</sup>, and even larger figures had been given by earlier investigators<sup>60-62</sup>. The HOMO-LUMO gap of Schwedhelm *et al.*, taken together with the HOMO offsets between PEN and  $C_{60}$  determined experimentally in References 56,57 would put  $\Delta_{LH}$  outside the region that could give enhanced QE.

In summary, we have presented a careful theoretical analysis of the PEN- $C_{60}$  interface within the correlated  $\pi$ -electron PPP model that is able to reproduce many of the experimental features of PEN and  $C_{60}$  quantitatively. We simulate solid state effects by independently varying parameters that change the energy separation  $\Delta_{LH}$  between the LUMO of  $C_{60}$  and the HOMO of PEN, and the many-body Coulomb interaction that contributes to the binding energy of the  $PEN^+C_{60}^-$  charge-transfer exciton. Based on these calculations we conclude that while it cannot be ruled out that SF is behind the high QE of the PEN- $C_{60}$  solar cell, neither is there unqualified support for this scenario from currently available experimental information. A variety of experiments have recently detected the charge-transfer exciton below the optical gap of the donor polymer in organic heterojunctions<sup>63-67</sup>. Interestingly, in all such cases the charge-transfer exciton has been found to occur at 1.3-1.6 eV, viz., significantly above the 0.9 eV where the  $PEN^+C_{60}^-$  charge-transfer exciton needs to occur for enhanced QE. We propose similar measurements for the detection of  $CTX_0$  in PEN- $C_{60}$ . In particular, direct photoexcitation of  $CTX_0$  has been possible in spite of its low oscillator strength<sup>65</sup>. We propose that experiments be performed on the PEN- $C_{60}$



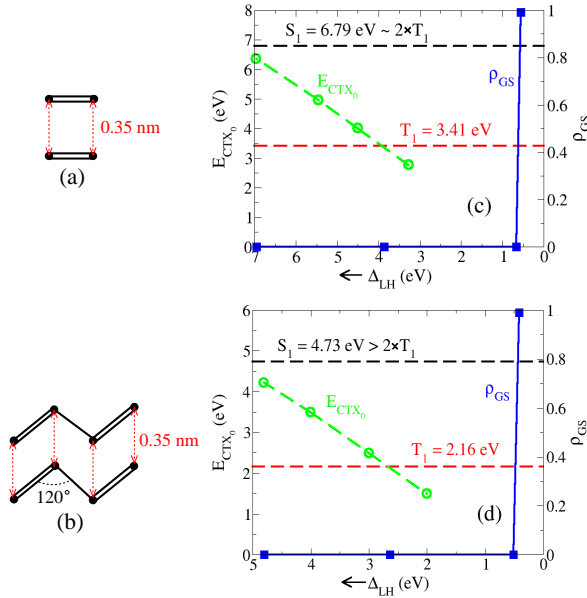


FIG. 4: (Color online) (a) and (b): Interacting pairs of ethylene-like and butadiene-like molecules, with Coulomb parameters chosen such that the lowest molecular triplet is nearly at half the energy of the optical singlet. MO offsets created artificially generate  $D$ - $A$  systems in both cases. (c) and (d):  $E_{CTX_0}$  and the ground-state ionicity  $\rho_{GS}$  versus the MO offset, for the systems in (a) and (b), respectively.

heterojunctions to detect the charge-transfer exciton directly.

### Acknowledgment

We are grateful to Professors Bernard Kippen (Georgia Tech), Oliver Monti (University of Arizona) and Zeev Valy Vardeny (University of Utah) for many helpful discussions. We thank Dr. Jérôme Cornil for bringing Reference 39 to our attention. This work was supported by NSF Grant No. CHE-1151475.

### Appendix: Higher Efficiency versus Ground-State Charge-Transfer

The SCI using HF basis assumes closed shell MOs as the ground-state. It is conceivable that as  $\Delta_{LH}$  continues to decrease, this assumption breaks down and the ground-state of the  $D$ - $A$  system becomes ionic, as has been observed in mixed-stack crystalline charge-transfer solids<sup>33</sup>. We have considered this possibility because a triplet state that is at half the energy of the singlet exciton is covalent in the valence-bond language<sup>21,22</sup>, and it is conceivable that before the ionic  $CTX_0$  can be below the covalent  $T_1$  the ground-state itself becomes predominantly ionic, which would have negative consequence for solar cell efficiency. Whether or not this happens cannot be checked within the HF approximation. To test whether the condition  $E_{CTX_0} \leq E_{T_1}$  can be satisfied without the ground-state becoming ionic we have done exact diagonalizations of our Hamiltonian for coupled hypothetical small molecules (see Figs. 4(a) and (b)). Our systems consist of pairs of molecules that resemble ethylene and butadiene, with the difference that we choose Coulomb parameters such that the triplet exciton is nearly at half the energy of the singlet optical exciton, while keeping all intramolecular and intermolecular electron hoppings realistic. This is achieved by taking  $U = 5.56$  eV and  $\kappa_{\perp} = \kappa = 1.7$  (which is not too far from realistic parameters). We include the site energy term in Eq. 2 for one of the two molecules in each case, thus breaking the symmetry and creating a  $D$ - $A$  system. We keep varying  $\Delta_{LH}$  slowly and monitor both  $E_{CTX_0}$  and the ground-state ionicity (the relative weight of the ionic configuration  $D^+A^-$  in the wavefunction)  $\rho_{GS}$ . Our results for the two cases are shown in Figs. 4(c) and (d). In both cases the ground-state continues to be covalent where  $E_{CTX_0} \leq E_{T_1}$  is reached, and the neutral-ionic transition occurs at a much smaller  $\Delta_{LH}$ . We have confirmed that this is true for other  $\kappa_{\perp}$  also. Essentially, as long as the intermolecular hopping integral has a weak role, as is necessarily true in real  $D$ - $A$  systems with  $C_{60}$  as the acceptor,  $E_{CTX_0} \leq E_{T_1}$  can be reached even with covalent ground-state.

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